GEOCHEMISTRY OF SHALLOW GROUND WATER IN THE FORT UNION FORMATION OF THE NORTHERN POWER RIVER BASIN, SOUTHEASTERN MONTANA

by

Roger W. Lee

Abstract. Shallow water in the coal-bearing Paleocene Fort Union Formation of southeastern Montana was investigated to provide a better understanding of the geochemistry. Springs, wells less than 200 feet deep, and wells greater than 200 feet deep were observed to have different water qualities. Overall, the ground water exists as two systems: a mosaic of shallow, chemically dynamic, and localized recharge-discharge cells superimposed on a deeper, chemically static regional system. Water chemistry is highly variable in the shallow system, whereas sodium and bicarbonate waters characterize the deeper system.

Within the shallow system, springs and wells less than 200 feet deep show predominately sodium and sulfate enrichment processes from recharge to discharge. These processes are consistent with the observed aquifer mineralogy and aqueous chemistry. However, intermittent mixing with downward moving recharge waters or upward moving deeper waters, and bacterially catalyzed sulfate reduction, may cause apparent reversals in these processes.

Introduction

Accelerated mining of shallow coal deposits in parts of the northern Powder River Basin of southeastern Montana has generated interest in hydrologic investigations because of the unknown impact on ground and surface waters. A major study of ground water in and around proposed coal-leasing tracts was begun by the U.S. Geological Survey in 1973 in cooperation with the Montana Bureau of Mines and Geology and the U.S. Bureau of Land Management. The purpose of this report is to describe the geochemistry of water from the Fort Union formation in the northern Powder River Basin (fig. 1). The results will be useful in defining the hydrologic setting of the basin prior to extensive mining, in developing hydrologic models of the shallow ground-water system, and in developing solute-transport and mass-transfer models of the ground-water quality.
Data collection in the study area began in December 1973. The initial work was primarily of an areal reconnaissance nature, consisting of the inventory of existing water wells and springs and the collection of water samples from selected sites. Chemical analysis of the water samples was performed by the laboratory of the Montana Bureau of Mines and Geology in Butte, Montana and the USGS National Water Quality Laboratory in Denver, Colo. On-site processing of samples collected for analysis differed for the two laboratories during the early part of the study. Prior to March 1, 1976, all samples sent to Butte were unfiltered and untreated. After this date, samples sent for analysis included unfiltered-untreated, filtered acidified, and filtered untreated. Samples sent to Denver throughout the study and to Butte after March 1, 1976, were processed according to standard sampling methods of Brown, Skougstad, and Fishman (1970). Temperature and specific conductance were measured on-site for all samples, and pH was measured in the field only on samples sent to Denver. All water quality data resulting from this investigation are contained in a report by Lee (1979).

**Geohydrologic Setting**

The northern Powder River Basin of southeastern Montana is part of a sedimentary basin whose upper units form a complex geohydrologic system. A detailed discussion of the geology of the area can be found in the report by Lewis and Roberts (1978). Principal aquifers occur in deposits of Late Cretaceous age as well as the overlying Fort Union Formation of...
Paleocene age.

Upper Cretaceous rocks (Hell Creek Formation) underlying the Fort Union Formation consist principally of shale and siltstone, locally interbedded with fine- to medium-grained sandstone containing thin coal beds. These rocks that directly underlie the Fort Union Formation are limited as a water supply. However, Cretaceous rocks lower in the stratigraphic section are reliable sources of water for artesian wells in and near the study area, and upward leakage of water from these rocks may influence the hydraulics and geochemistry of water in the Fort Union.

The Fort Union Formation is composed of, from deepest to shallowest, the Tullock Member, Lebo Shale Member, and Tongue River Member (fig. 2). The formation was deposited in a deltaic to estuarine environment, resulting in complex sedimentation characterized by lenticular beds, heterogeneous lithology, truncated units, and abrupt facies changes.

The Tullock member consists of interbedded shale, sandstone, siltstone, and thin but persistent coal beds in the lower part, grading upward to carbonaceous shale. Sandstones and coal beds provide small amounts of water to wells, which in some locations are artesian.

The Lebo Shale Member is predominantly shale containing interbeds of siltstone and thin coal beds, which may supply small quantities of water to a few wells.

The Tongue River Member occurs throughout most of the study area. It consists of flat-lying sandstone, siltstone, and numerous coal beds. Red, highly fractured clinker (overburden baked by coal combustion) occurs at the fringes of many of the coal beds at the land surface. Lateral subsurface penetrations of burns of as much as
1 mile from the original coal outcrop are apparent from the widespread occurrences of clinker. The Tongue River Member comprises the major shallow aquifer in the study area.

Alluvium, present in most of the stream valleys, is principally sand, silt, clay, and gravel lenses. This unit is a source of water in the valleys for domestic and stock use.

Aquifers within the Fort Union Formation in the study area have been previously described as being of two types: (1) an unconfined or water-table aquifer; and (2) a series of confined deep aquifers (U.S. Bureau of Land Management, 1975). The water table generally parallels the topography. Hydrologic data collected in the study area are being used in the preparation of a potentiometric-surface map. The data are on file in the Geological Survey district office, Helena, Montana.

**Geochemistry of Shallow Ground Water**

Chemical analyses of water from wells and springs in the Powder River Basin indicate a wide range in concentrations of dissolved species. Table 1 summarizes the chemical data according to source and depth.

<table>
<thead>
<tr>
<th>Source of water</th>
<th>Number of samples</th>
<th>Statistic category</th>
<th>Calcium (Ca)</th>
<th>Magnesium (Mg)</th>
<th>Sodium (Na)</th>
<th>Potassium (K)</th>
<th>Bicarbonate (HCO₃⁻)</th>
<th>Carbonate (CO₃²⁻)</th>
<th>Sulfate (SO₄²⁻)</th>
<th>Chloride (Cl⁻)</th>
<th>Dissolved solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Springs</td>
<td>149</td>
<td>Minimum</td>
<td>9.5</td>
<td>3.0</td>
<td>6.5</td>
<td>2</td>
<td>5</td>
<td>0</td>
<td>15</td>
<td>1.3</td>
<td>166</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>110</td>
<td>140</td>
<td>246</td>
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<td>686</td>
<td>2</td>
<td>830</td>
<td>8.0</td>
<td>1,638</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Maximum</td>
<td>440</td>
<td>510</td>
<td>1,800</td>
<td>51</td>
<td>1,600</td>
<td>87</td>
<td>8,500</td>
<td>26</td>
<td>5,200</td>
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<tr>
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<td>275</td>
<td>Minimum</td>
<td>1.7</td>
<td>.3</td>
<td>3.2</td>
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<td>20</td>
<td>0</td>
<td>3</td>
<td>0.4</td>
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<td>less than</td>
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<td>Mean</td>
<td>120</td>
<td>120</td>
<td>410</td>
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<td>200 feet.</td>
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<td>Maximum</td>
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<td>680</td>
<td>1,800</td>
<td>48</td>
<td>2,000</td>
<td>53</td>
<td>4,400</td>
<td>120</td>
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<td>141</td>
<td>Minimum</td>
<td>1.0</td>
<td>.1</td>
<td>13</td>
<td>1</td>
<td>250</td>
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<td>290</td>
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<tr>
<td>greater than</td>
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<td>Mean</td>
<td>32</td>
<td>27</td>
<td>450</td>
<td>4</td>
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<td>14</td>
<td>360</td>
<td>36</td>
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</tr>
<tr>
<td>200 feet.</td>
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<td>Maximum</td>
<td>350</td>
<td>350</td>
<td>1,700</td>
<td>14</td>
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<td>440</td>
<td>3,300</td>
<td>770</td>
<td>5,720</td>
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Waters from shallow wells (generally less than 200 feet deep) at higher altitudes, and most springs, are usually dominated by magnesium, calcium, sodium, bicarbonate and sulfate ions, and small concentrations of chloride. Waters from shallow wells at the lower altitudes either are dominant in sodium and sulfate with lower concentrations of magnesium, calcium, and bicarbonate, or are dominant in sodium and bicarbonate with lower concentrations of magnesium, calcium, and sulfate. Chloride concentrations are small from springs or wells less than 200 feet deep (8 and 13 mg/L, respectively) but increase to an average concentration of 36 mg/L in some wells deeper than 200 feet.

Water quality appears to differ with depth, as illustrated on the Piper (1953) trilinear diagram (fig. 3). Water from wells deeper than 200 feet is generally dominated by sodium and bicarbonate, often with chloride concentration greater than for shallower aquifers (table 1). Water quality at depths greater than 200 feet is generally less variable than at shallower depths. Thus, water appears to be chemically stratified—a shallow, dynamic geochemical system above a static regional one.

Geochemical maps (figs. 4-7) were constructed to illustrate chemical trends and gradients in the shallow system. The maps are based on data from springs and wells less than 200 feet deep in areas of greatest data availability.

TABLE 1.—Summary of selected chemical constituents in water from wells and springs

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<tr>
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<td>5,720</td>
</tr>
</tbody>
</table>

Increases and decreases in the ratio of sodium plus potassium to total cations for much of the study area are illustrated on figures 4, 5. The values are based on the following equation,
Radius of circle indicates dissolved-solids concentration, in milligrams per liter.

\[ \text{Percent Na} + \text{K} = \frac{Na + K}{Na + K + Ca + Mg} \times 100 \]

The maps (figs. 4, 5) suggest the presence of numerous localized geochemical cells. The chemical quality appears to change as ground water flows from areas of low percent sodium plus potassium, generally recharge areas to areas of high percent sodium plus potassium, generally discharge areas, to areas of high percent sodium.

**TABLE 2.—Representative saturation indices from WATEQF**

[Location number based on Federal system of land subdivision. The first numeral and letter indicate the township; the second, the range; and the third, the section. The first letter following the section number denotes the 100-acre tract; the second, the 40-acre tract; the third, the 10-acre tract; and the fourth, the 2½-acre tract. Letters are assigned in a counterclockwise direction, beginning with "A" in the northeast quadrant. When more than one well or spring is located within a 2-acre tract, sequential numbers are added, starting with 1.]

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Saturation index for water from shallow wells</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stone 2N39E25ACDC</td>
<td>5S46E94DACA 7S39E35DABB 8S45E16DABC 8S45E16DABC2</td>
</tr>
<tr>
<td>Albite (NaAlSi3O8)</td>
<td>0.18 0.68 -0.88 0.77 -0.01</td>
</tr>
<tr>
<td>Aragonite (CaCO3)</td>
<td>0.46 -0.64 -0.74 -0.82 -0.91</td>
</tr>
<tr>
<td>Calcite (CaCO3)</td>
<td>0.36 0.30 -0.14 -0.20 0.07</td>
</tr>
<tr>
<td>Dolomite (CaMg(CO3)2)</td>
<td>1.07 0.88 -0.24 -0.14 0.15</td>
</tr>
<tr>
<td>Gypsum (CaSO4·2H2O)</td>
<td>-0.01 -0.74 -1.75 -0.72 -2.38</td>
</tr>
<tr>
<td>Magnesite (MgCO3)</td>
<td>0.42 0.39 -0.39 -0.25 -0.21</td>
</tr>
<tr>
<td>Natrolite (NaHCO3)</td>
<td>-3.16 -3.39 -4.71 -2.47 -2.57</td>
</tr>
</tbody>
</table>
plus potassium, generally discharge areas containing water that has been in contact with the rocks for a long time.

Increases and decreases in the ratio of sulfate to anions are illustrated on figures 5, 7. The percent values are based on equation 2, with all data in milliequivalents per liter.

\[
\text{Percent } \text{SO}_4 = \frac{\text{SO}_4}{\text{SO}_4 + \text{HCO}_3 + \text{CO}_3} \times 100
\]

Like sodium plus potassium, sulfate appears as geochemical cells and has similar gradients. However, several areas have trends in percent sulfate that are opposite to those for percent sodium plus potassium.

The maps show the diverse quality of shallow ground water in the study area. Major dissolved constituents vary moderately in some areas, whereas large variations are observed in other areas. Discussions of the changes observed in the chemical data along flow paths are essential to an understanding of the geochemical changes occurring in the shallow ground-water systems.

A flow path is the course of water flow in an aquifer down the hydraulic gradient. Chemical data for points along the flow path can demonstrate changes in solutes that occur with time and distance of travel as water flows downgradient. Stiff (1951) diagrams, which represent individual chemical analyses of major solutes in milliequivalents per liter, are used to illustrate the water quality.

Flow path A'-A (fig. 6) illustrates the most general solute change wherein sodium plus potassium and sulfate increase downgradient. Relatively small differences in solutes are observed from well 1 to well 2 as magnesium and calcium decrease and sodium plus potassium increases, with little change in anions. Stiff diagrams at well 2 and well 3, however, show significant increases in sodium plus potassium, sulfate, and dissolved solids (which is proportional to total milliequivalents) with minor changes in calcium, magnesium, and bicarbonate plus carbonate as the water moves downgradient. The concentration and change in concentration of chloride are not significant. Sodium and sulfate dominance in the shallow ground water, especially near discharge area, agrees with conclusions of other studies that indicate high concentrations of sulfate in the ground-water contribution to base flow of major streams in the study area (Knapton and McKinley, 1977).

Sodium plus potassium and sulfate enrichment appear to be reversed along flow path B'-B (fig. 9). Sodium plus potassium, magnesium, sulfate, and dissolved solids decrease significantly from well 4 to well 5, whereas calcium and bicarbonate remain fairly constant. Recharge water dominated by calcium and bicarbonate ions and very low in dissolved solids could have mixed with shallow ground water between well 4 and well 5.

A third type of geochemical trend is indicated along flow path C'-C (fig. 10). Sodium plus potassium, calcium, and magnesium show only slight decreases from the spring to well 6, with the major changes occurring in the anions as sulfate decreases and bicarbonate increases. From well 6 to well 7, calcium, magnesium, and sulfate decrease significantly. Although mixing of shallow waters with deeper sodium bicarbonate waters is indicated, chemical reactions involving loss of calcium and magnesium from solution and a change of bicarbonate for sulfate must also be considered plausible.

The concentrations of solutes in the shallow ground water are largely due to aquifer mineralogy and solution chemistry. Drill-hole core data from the Tongue River Member at Hanging Woman Creek in the southern part of the study area showed that sandstone, siltstone, and shale contain varying amounts of quartz (SiO2), coligoclase and adularia (sodium feldspars), calcite (CaCO3), dolomite (CaMg(CO3)2), aragonite (CaCO3), pyrite (FeS2), siderite (FeCO3), gypsum (CaSO4•2H2O), and clay minerals such as smectite, chlorite, illite, and kaolinite (Ebens, R.J., and Hinkley, T.K., USGS, written commun., 1977). This
FIGURE 4. - MAP SHOWING PERCENT SODIUM PLUS POTASSIUM IN SHALLOW WATER OF THE FORT UNION FORMATION, CENTRAL PART OF THE NORTHERN POWDER RIVER BASIN, SOUTHEASTERN MONTANA
FIGURE 5.—MAP SHOWING PERCENT SODIUM PLUS POTASSIUM IN SHALLOW WATER OF THE FORT UNION FORMATION, SOUTHERN PART OF THE NORTHERN POWDER RIVER BASIN, SOUTHEASTERN MONTANA
FIGURE 6.--MAP SHOWING PERCENT SULFATE IN SHALLOW WATER OF THE FORT UNION FORMATION, CENTRAL PART OF THE NORTHERN POWDER RIVER BASIN, SOUTHEASTERN MONTANA
Figure 7.-Map showing percent sulfate in shallow water of the Fort Union Formation, southern part of the northern Powder River Basin, southeastern Montana.
Figure 8.—Hydrologic section for flow path A'-A in the central part of the study area. Lines of section on plates 1 and 2.

Information, coupled with saturation index calculations from the computer program WATEQF (Plummer and others, 1976), provides insight into the geochemistry.

Saturation indices for significant minerals from five water-quality analyses are given in table 2. The analyses were selected as representative of WATEQF calculations for water-quality analyses distributed throughout the study area. Positive values of saturation index (log IAP/KT) imply supersaturation, negative values indicate undersaturation, and values approaching zero show saturation or nearly so. Saturation or supersaturation suggests the possible presence of a particular mineral in the aquifer.

Some of the samples (7S39E35DABB and 8S45E16DBCB) indicate a general undersaturation with respect to the common sedimentary minerals in table 2. Many of the water samples (2N39E25ACDC, 5S46EO4DACA, and 8S45E16DBCB2) indicate saturation with at least one of the carbonate minerals (calcite, aragonite, or dolomite). Sodium feldspar (albite) usually shows aqueous phase saturation or supersaturation. Gypsum saturation is rarely approached, as in 2N39E25ADC. Highly soluble species, such as nahcolite (table 2) and sodium and magnesium sulfate salts, which are not observed in the mineral phase in the aquifer, always show undersaturation; this indicates the high capacity of ground water to become enriched in these dissolved species. The presence of sodium feldspar, calcite, aragonite, and dolomite is supported by both aqueous phase equilibrium data and mineralogic data. From the chemical equilibrium data and the limited mineralogic information major chemical reactions occurring in the shallow subsurface of the study area can be postulated.

The proportion of sodium plus potassium to
total cations in the shallow ground water can increase (sodium enrichment) or decrease (sodium depletion) as illustrated by figures 4-5, 8-10. The chemical reactions causing the changes can be classified as direct enrichment, cation exchange, or indirect enrichment.

Direct enrichment occurs when sodium is directly leached from the sediments as in equation 3 (Stumm and Morgan, 1970):

$$9\text{H}_2\text{O} + 2\text{H}_2\text{CO}_3 + 2\text{NaA}_1\text{Si}_3\text{O}_8 \leftrightarrow (\text{ albite})$$

$$2\text{Na}^+ + 2\text{HCO}_3^- + 4\text{H}_4\text{SiO}_4 + \text{A}_1\text{2Si}_2\text{O}_5(\text{OH})_4$$ (kaolinite)

Cation exchange (eq 4) is a process whereby sodium ions are exchanged for calcium and magnesium ions, usually by clay minerals:

$$\text{Ca}^{++} + \text{Mg}^{++} + 4\text{Na}^+ (\text{sediment}) \leftrightarrow$$ (4)

$$\text{Ca, Mg (sediment)} + 4\text{Na}^+ \quad \text{Ca, Mg (sediment)} + 4\text{Na}^+ \quad \text{Ca, Mg (sediment)} + 4\text{Na}^+$$

Indirect enrichment of sodium occurs when magnesium or calcium ions in solution are precipitated as in equations 5-7 (Hem, 1970):

$$\text{Ca}^{++} + \text{HCO}_3^- \leftrightarrow \text{CaCO}_3 + \text{H}^+ \quad \text{(5)}$$

$$\text{Mg}^{++} + \text{HCO}_3^- \leftrightarrow \text{MgCO}_3 + \text{H}^+ \quad \text{(6)}$$

$$\text{Ca}^{++} + \text{Mg}^{++} + 2\text{HCO}_3^- \leftrightarrow \text{(7)}$$

$$\text{Ca, Mg(CO}_3)_2 + 2\text{H}^+$$

These reactions (eq 3-7) are all reversible. If they occur from left to right as written, relative enrichment in sodium results. However, if they occur from right to left, relative depletion in sodium results.

Sodium depletion also could occur by dilution whereby water containing a lower amount of
sodium mixes with water containing a large amount of sodium. This process would generally occur in recharge areas where water percolating through soils and the unsaturated zone contains higher percentages of calcium and magnesium than waters farther downgradient.

Among the anions, sulfate and bicarbonate plus carbonate provide the major competition for dominance in solution. Chloride is significant in deeper Cretaceous aquifers and may be noteworthy in some areas where upward movement of these waters into the shallow system is possible.

Sulfate enrichment is the dominant chemical process in the shallow system although bicarbonate may dominate at recharge areas. Direct sulfate enrichment may occur from weathering of pyrite (Stumm and Morgan, 1970) or dissolution of gypsum (eqs 8 and 9) although gypsum dissolution is most likely.

\[
2 \text{FeS}_2 + 7 \text{O}_2 + 2\text{H}_2\text{O} \leftrightarrow 2\text{Fe}^{+++} + 4\text{SO}_4^{2-} + 4\text{H}^+ \quad (8)
\]
\[
\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \leftrightarrow \text{Ca}^{++} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \quad (9)
\]

Direct increases in sulfate by the reactions shown in equations 8 and 9 usually relate to increases in dissolved solids. Indirect increases in sulfate may occur via chemical precipitation of calcium and magnesium carbonates (eqs 5-7), effectively removing bicarbonate from solution.

The apparent loss of sulfate in the aqueous phase down a flow path (depletion) in many instances may be caused by mixing of sulfate-laden water with low-sulfate recharge waters or with low-sulfate waters of deeper aquifers, although the lack of change in chloride.
concentration could rule out the latter. Another possible mechanism involves the bacterially promoted reduction of sulfate progressively down the flow path (Goldhaber and Kaplan, 1974).

\[
\text{sulfate-reducing bacteria} \quad SO_4^{2-} + CH_4 (\text{organic matter}) \rightarrow HS^- + HCO_3^- + H_2O \quad (10)
\]

Anaerobic bacteria, which reduce sulfate to sulfide, have been identified in ground waters in the study area. The extent and variability of this process are presently unknown, but further work is planned to enhance understanding of this mechanism.

The reduction of sulfate and the conversion of organic carbon to bicarbonate may explain the higher percentage of bicarbonate in the deeper, confined ground waters in the study area. The sulfate-reduction mechanism may have been the dominant process acting on these waters and the resulting sodium bicarbonate water could be an ultimate water quality in these sediments.

Using sodium enrichment or depletion, and sulfate enrichment or depletion, as arbitrary reference trends of major cations and anions respectively (figs. 4-7), geochemical concepts can be applied to the observed phenomena. Causes and effects are shown in table 3.

Four mechanisms for the water-quality trends observed on figures 4-7 are possible, if the system is assumed to be dynamic rather than static (which would exclude instances of no change in percent sodium plus potassium or percent sulfate):

1. Na $\uparrow$ SO$_4$ $\uparrow$ -- most commonly observed
2. Na $\uparrow$ SO$_4$ $\downarrow$ -- most commonly observed
3. Na $\downarrow$ SO$_4$ $\uparrow$ -- not commonly observed
4. Na $\downarrow$ SO$_4$ $\downarrow$ -- observed

Processes 1, 2, and 4 would represent nearly all the conditions observed in the project area and indicated on the water-quality maps. Process 3 is not likely because a major "sink" for sodium has not been identified or observed in the study area.

**Conceptual Model**

The various observed water-quality phenomena were used to construct a recharge-discharge conceptual model of the shallow ground-water system (fig. 11). The vertical scale may be exaggerated as much as 50 times the horizontal scale. The distance from divide to stream may range from 2 to 20 miles. Often, however, the systems are highly localized, with significant solute changes occurring over small distances (1-5 miles).

At point $A$, water quality would represent recharge waters dominated by magnesium, calcium, and bicarbonate, with significant amounts of sodium and sulfate, but low in dissolved solids. As the water percolates through the systems, sodium and sulfate enrichment results in higher percentages of sodium, sulfate, and dissolved solids at $B$.

At point $C$, water quality would represent a mixture of an intermediate sodium and sulfate water, and recharge water that has percolated through the highly permeable clinker facies. The mixing results in a lower dissolved-solids solution than at with the water chemistry approaching that for recharge water. At $D$, water quality is predominantly sodium and sulfate (developed by sodium and sulfate enrichment), which may discharge as base flow to the stream. In the deep coal at $E$, sulfate reduction may dominate the geochemistry of the ground water, producing a sodium bicarbonate water distinguishable with difficulty from water of the deeper aquifers. At $E$, static water of the deeper regional systems (whose chemical character probably developed similar to water at $E$) would be dominated by sodium and bicarbonate. Finally at $G$, upward leakage would result in a water that is a composite of waters from $D$, $E$, and $F$. Chemical character of water at $G$ would be determined by the dominant water supply from $D$, $E$, or $F$. 


Table 3.—Geochemical Processes

<table>
<thead>
<tr>
<th>Sodium enrichment (Na⁺)</th>
<th>Sodium depletion (Na⁺)</th>
<th>Sulfate enrichment (SO₄²⁻)</th>
<th>Sulfate depletion (SO₄²⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIRECT</td>
<td>DILUTION</td>
<td>DIRECT</td>
<td>DILUTION</td>
</tr>
<tr>
<td>Reaction of equation 3.</td>
<td>CATION EXCHANGE</td>
<td>Reaction of equation 8,</td>
<td>DIRECT</td>
</tr>
<tr>
<td>CATION EXCHANGE</td>
<td>Reaction of equation 4.</td>
<td>reversed.</td>
<td>reaction of equation 9,</td>
</tr>
<tr>
<td>INDIRECT</td>
<td>INDIRECT</td>
<td>Reactions of equations 5-7.</td>
<td>INDIRECT</td>
</tr>
<tr>
<td>Reactions of equations 5-7.</td>
<td>DIRECT</td>
<td>Reaction of equation 9,</td>
<td>BACTERIAL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>reversed.</td>
<td>Reaction of equation 10.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>INDIRECT</td>
<td>INDIRECT</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Reactions of equations 5-7.</td>
<td></td>
</tr>
</tbody>
</table>

Conclusions

Chemical data from ground water in the northern Powder River Basin indicate the presence of two distinct geochemical systems. The shallow system is generally less than 200 feet deep, is localized, and consists of groups of dynamic geochemical cells. The underlying system is greater than 200 feet deep, regional in extent, and chemically static.

Water chemistry generally differs between the shallow and deep systems. Water from wells in the shallow system at high altitudes and from springs is generally dominant in magnesium, calcium, sodium, and bicarbonate, with moderate amounts of sulfate and low concentrations of chloride. These are probably recharge waters. Water from wells in the shallow system at lower altitudes either is dominant in sodium and sulfate with lower values of magnesium, calcium, and bicarbonate, or is dominant in sodium and bicarbonate with lower values of magnesium, calcium, and sulfate. Water from the deep system is dominant in sodium and bicarbonate with some locally significant amounts of chloride.

Geochemical changes occur as water within the shallow system flows from areas of recharge to areas of discharge. Aquifer mineralogy and solution chemistry are largely responsible for the observed concentrations of solutes, although such variables as time, distance of travel, and hydrogeology are also important. The principal chemical reactions that in combination result in higher percent sodium and percent sulfate as water moves downgradient are (1) dissolution of calcite, dolomite, aragonite, sodium feldspars (oligoclase), pyrite, and gypsum by percolating recharge waters combined with (2) the reaction of cation exchange on clay minerals. Bacterially induced sulfate reduction may cause the observed sulfate decreases in ground water. Other minerals and other chemical reactions may be present in the system, but are of limited significance to the observed water quality.
Geochemical changes within the shallow system also occur as a result of mixing of ground waters. Percolating recharge waters may mix with older ground waters, effectively reducing the percent sodium and percent sulfate in the aquifers. Data have shown that water in deep aquifers can locally leak into the shallow system, causing a decrease in percent sulfate and a slight increase in chloride content.

The observed water-quality phenomena were used to construct a generalized conceptual model of the shallow ground-water system in southeastern Montana. The model shows water qualities resulting from recharge, enrichment, mixing, and reducing conditions.

Selected References


___1977 a, Resource and potential reclamation evaluation of Bear Creek study area, West Moorhead coalfield, Montana: EMRIA report No. 8, 148 p.

___1977b, Resource and potential reclamation evaluation of Hanging Woman Creek study area: EMRIA report No. 12, 309 p. [1978].